

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES  
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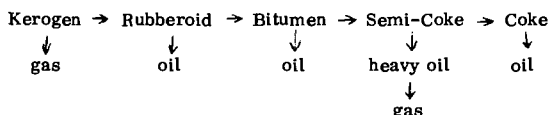
ANALYSIS OF PYROLYSIS KINETICS OF EASTERN OIL SHALES

By

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INTRODUCTION

The kinetics of pyrolysis of Western oil shale has been studied by a number of investigators (1-6). Several reaction mechanisms have been proposed to account for the pyrolysis kinetics of Colorado shale. Hubbard and Robinson (4) postulated a two-step mechanism for the decomposition of kerogen to bitumen and subsequently bitumen to oil and gas. Johnson, et al. (5) concluded the following mechanism which was partially verified with experimental data:



Details of these mechanisms were documented in a review by Fisher (6). Relatively little is known regarding the pyrolysis kinetics of Eastern shale. The present work was undertaken to measure the rate of organic matter decomposition during pyrolysis of Kentucky Sunbury oil shale. Thermoanalytical methods are used to obtain the kinetics data. It should be noted, however, that the thermogravimetric analyzer (TGA) utilized in the present experiment is not equipped with G. C. or I. R. for gas composition measurement. Only the weight variation can be obtained from the TGA. Thus, the model developed here is only for the weight variation of solid reactants in the course of pyrolysis. Furthermore, the proposed model does not require consideration of the activation energy distribution function for the reactions. By heating the oil shale, gaseous and liquid products are formed which result from the many different reactions involving these components. The reported pyrolysis kinetics are, thus, an average for these many different reactions that take place. The representation of the decomposition rate would become very complex if all the mechanistic reactions were to be identified and accounted for. Thus, a global first order rate expression is assumed for simplicity's sake (2, 3, 7). For this reason, the activation energy and the frequency factor are the only "representative" kinetic values for a complicated reaction system. These values are, however, useful from the engineering standpoint of oil shale retorting and can be used in a mathematical model to represent the process.

EXPERIMENTAL

The oil shale used in the present study was Kentucky Sunbury shale. Ultimate analysis (wt %) of the oil shale: hydrogen - 1.55; nitrogen - 0.53; sulfur - 3.41; total carbon - 14.07; oxygen - 3.30; moisture - 2.18; ash - 74.96; with a Fischer Assay oil yield 9.3 gallons/ton. The samples were crushed and sieved to 16/20 U. S. mesh.

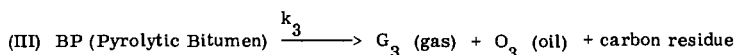
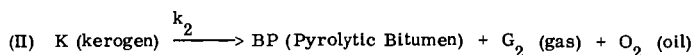
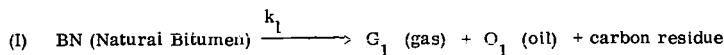
A Du Pont 951 thermogravimetric balance interfaced to a Du Pont 1090 thermal analyzer was used to obtain the weight-loss data as a function of time and temperature. The TGA experiments were carried out by heating the sample from ambient temperature to 600°C. The heating rates of 5°, 10°, 15° and 20°C/min were employed. Differential scanning calorimetric (DSC) data were obtained with a Du Pont cell base and the 1090 thermal analyzer. An aluminium pan containing the sample was placed on the raised platform in the DSC cell and an empty pan was placed on the reference platform. A known weight of sample was subjected to a linear heating rate in a flow of nitrogen or CO<sub>2</sub>. DSC scans for the samples were obtained from 150° to 600°C at a linear heating rate of 10°C/min. A non-isothermal technique was utilized for determining the kinetics of oil shale pyrolysis.

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## RESULTS AND ANALYSIS

Scrima, et al. (8) compared the bitumen removed thermally from oil shale (the shale sample was heated to 300°C at 28°C/min) with those removed by benzene extraction. Based on thermal chromatography of Green River oil shale, the two chromatograms appear identical, demonstrating that natural bitumen could be thermally removed at about 300°C.

Consider the following pyrolysis mechanism for oil shale which consists of two decomposable materials, i. e., bitumen (natural) and kerogen:



Reaction (I) takes place at a temperature from 100°C to 300°C and reactions (II) and (III) take place at temperatures beyond 300°C. Assuming first order kinetics for each step of reaction, we have

$$\frac{dW_{BN}}{dt} = -k_1 W_{BN} \quad 1)$$

$$\frac{dW_k}{dt} = -k_2 W_k \quad 2)$$

$$\frac{dW_{BP}}{dt} = k_2 f W_k - k_3 W_{BP} \quad 3)$$

where  $W_{BN}$ ,  $W_k$  and  $W_{BP}$  are the weight of natural bitumen, kerogen and pyrolytic bitumen, respectively;  $f$  is the weight fraction of the decomposed kerogen which yields bitumen (2).

For a non-isothermal reaction condition in which the heating rate is linear, we have

$$\frac{dT}{dt} = Hr \quad 4)$$

where  $Hr$  is the heating rate. Equations 1 through 3 yield

$$\frac{dW_{BN}}{dt} = \frac{-k_1}{Hr} W_{BN} \quad 5)$$

$$\frac{dW_k}{dT} = \frac{-k_2}{Hr} = W_k \quad 6)$$

$$\frac{dW_{BP}}{dT} = \frac{1}{Hr} (k_2 f W_k - k_3 W_{BP}) \quad 7)$$

The Arrhenius forms for the variation of  $k_1$ ,  $k_2$ ,  $k_3$  with temperature are

$$k_1 = k_{10} \exp \left( \frac{-E_1}{RT} \right) \quad 8)$$

$$k_2 = k_{20} \exp \left( \frac{-E_2}{RT} \right) \quad 9)$$

$$k_3 = k_{30} \exp \left( \frac{-E_3}{RT} \right) \quad 10)$$

Thus, Equations 5 through 7 can be rewritten as

$$\frac{dw_{BN}}{dT} = - \frac{k_{10}}{Hr} \exp \left( \frac{-E_1}{RT} \right) W_{BN} \quad (11)$$

$$\frac{dw_{BN}}{dT} = - \frac{k_{20}}{Hr} \exp \left( \frac{-E_2}{RT} \right) W_k \quad (12)$$

$$\frac{dw_{BP}}{dT} = \frac{1}{Hr} \left( k_{20} \exp \frac{-E_2}{RT} f W_k - k_{30} \exp \frac{-E_3}{RT} W_{BP} \right) \quad (13)$$

The boundary conditions for Equations 11 through 13 are, respectively,

$$T = 100^\circ\text{C}: W_{BN} = W_{BNO}; T = 300^\circ\text{C}: W_k = W_{k0}, W_{BP} = 0. \quad (14)$$

The total weight of the sample  $W$  is related to  $W_{BN}$ ,  $W_k$  and  $W_{BP}$  by

$$W = W_i + W_{BN} + W_k + W_{BP}. \quad (15)$$

Equations 11 through 13 subject to the boundary conditions of Equation 14 require a numerical scheme for solution.

Figure 1 shows an oil shale thermal histogram of weight loss and derivative weight loss versus temperature in a nitrogen flow at a heating rate of  $5^\circ\text{C}/\text{min}$ . There are two major peaks from the derivative weight loss - temperature curve. The first peak begins about  $20^\circ\text{C}$  and ends about  $100^\circ\text{C}$  while the second peak begins about  $350^\circ\text{C}$  and ends about  $550^\circ\text{C}$ . It is likely that the first peak represents the devolatilization of water, while the second peak represents the decomposition of pyrolytic bitumen. The differential weight variation between two peaks is considered to be the decomposition of natural bitumen and kerogen. The natural bitumen was extracted by benzene and the weight percent of natural bitumen in the oil shale was measured to be  $\sim 2\%$ . There is about 2% weight loss which occurred from  $100^\circ\text{C}$  to  $\sim 300^\circ\text{C}$ . This weight loss suggests that nearly all the natural bitumen decomposes in this low temperature range. Similarly, Figures 2, 3 and 4 show the histograms of weight loss and derivative weight loss versus temperature for the heating rate of  $10^\circ\text{C}/\text{min}$ ,  $15^\circ\text{C}/\text{min}$  and  $20^\circ\text{C}/\text{min}$ , respectively. The heating rate has moderate effects on the variation of weight loss. The results indicate the systematic shift in the rate maxima to lower temperatures with decreasing heating rate. Figures 5 and 6 summarize the experimental results on extent of conversion over the temperature range  $165^\circ\text{C}$  to  $280^\circ\text{C}$  and  $365^\circ\text{C}$  to  $550^\circ\text{C}$ , respectively.

The experimental results given in Figures 1 through 4 support the basic pyrolysis mechanism proposed in the present kinetics study. Figures 1 through 4 also show the comparison between the model prediction and the experimental data for the weight loss-versus-temperature relationship. The frequency factor and activation energy based on the best fit of the model to the experimental data are found to be

$$k_{10} = 1,040 \text{ 1/min}; E_1 = 33.5 \text{ kJ/mole}$$

$$k_{20} = 900 \text{ 1/min}; E_2 = 41.9 \text{ kJ/mole}$$

$$k_{30} = 1.2 \times 10^{12} \text{ 1/min}; E_3 = 173.7 \text{ kJ/mole}$$

$$f = 0.9$$

Note that in the calculation based on the model, the weight loss due to water devolatilization is assumed to be known. As can be seen from these figures, the comparison is satisfactory. The closeness of the fit is a good indication of the adequacy of assuming a first order decomposition mechanism. It is noted that the values for frequency factor and activation energy obtained for kerogen decomposition are comparable to those reported for Colorado oil shale (2, 3, 5, 7).

Figure 7 shows DSC thermal histogram. The data were analyzed by Borchardt/Daniels DSC Kinetics (1957) Program. A reaction order of 0.88 with  $E_3 = 151 \text{ kJ/mole}$  were obtained.  $E_3$  would be  $160 \text{ kJ/mole}$  assuming a first order reaction. These results compare favorably with TGA

Sample: KENTUCKY SHALE  
 Size: 60.32 mg  
 Rate: 5 DEG/MIN 100CC N2/MIN

TGA

Date: 8-Oct-83 Time: 11:50:57  
 File: SUNBURY.01  
 Operator: M. SHEN

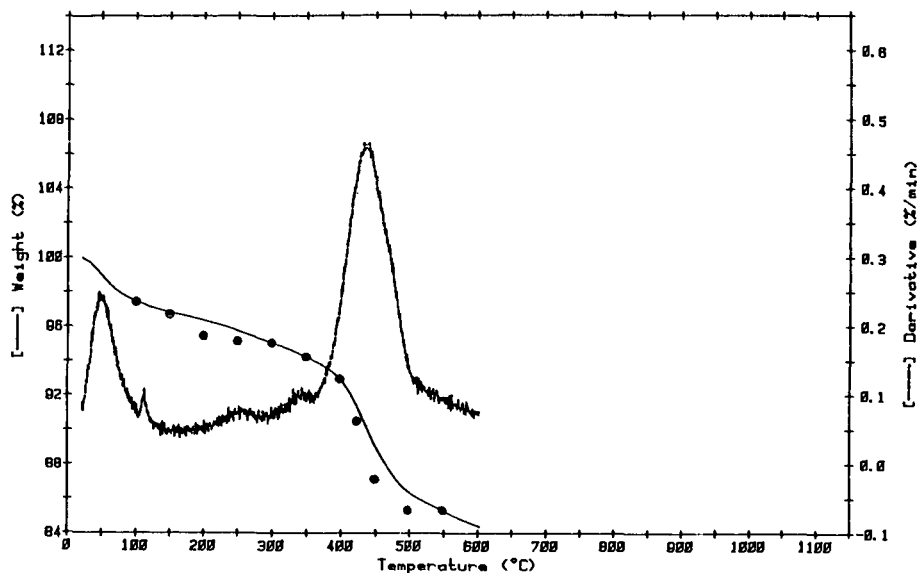


Figure 1. Non-isothermal histogram of weight loss versus temperature at 5°C/min.

Sample: KENTUCKY SHALE  
 Size: 59.96 mg  
 Rate: 10 DEG/MIN 100CC N2/MIN

TGA

Date: 6-Oct-83 Time: 22:45:45  
 File: SUNBURY.07  
 Operator: M. SHEN

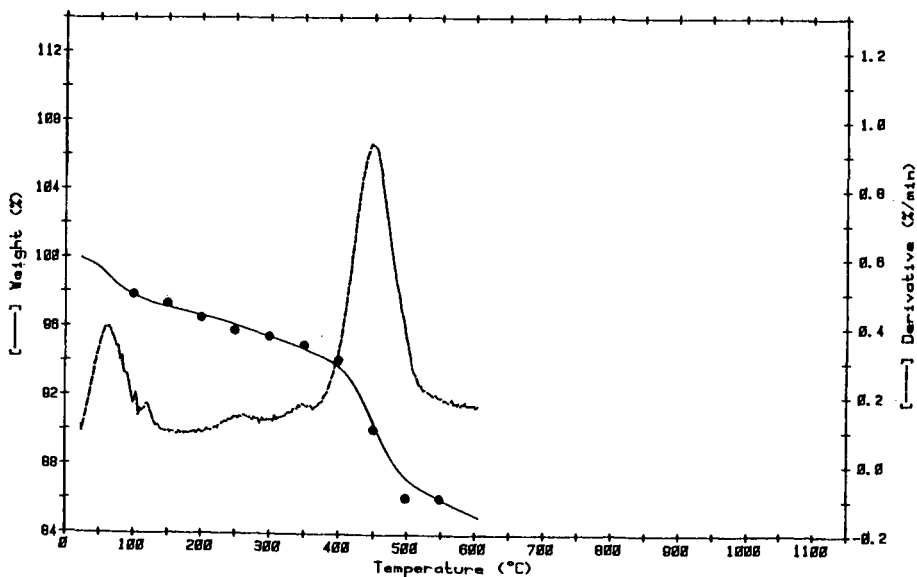


Figure 2 Non-isothermal histogram of weight loss versus temperature at 10°C/min

Sample: KENTUCKY SHALE  
 Size: 60.55 mg  
 Rate: 15 DEG/MIN 100CC N2/MIN

TGA

Date: 6-Oct-83 Time: 20:50:12  
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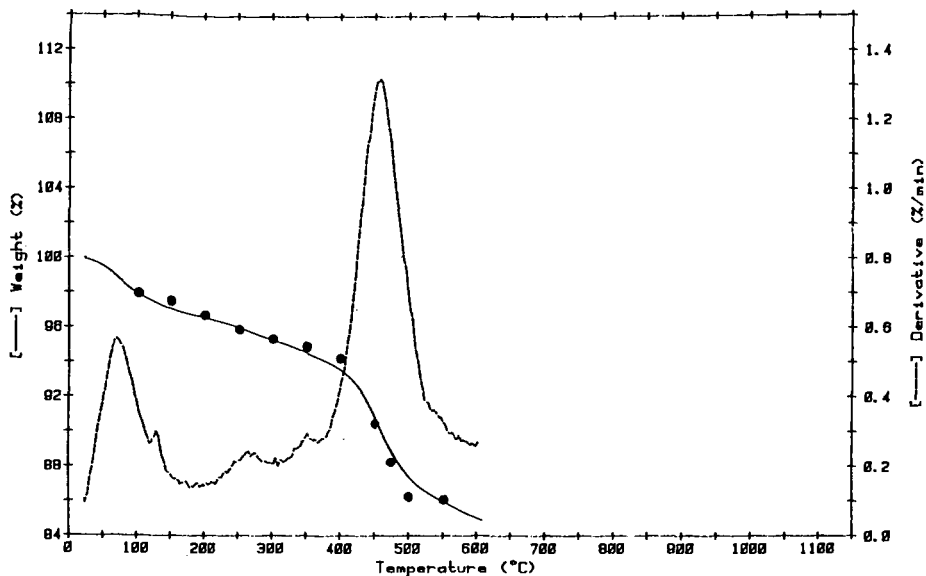


Figure 3 Non-isothermal histogram of weight loss versus temperature at 15°C/min

Sample: KENTUCKY SHALE  
 Size: 60.03 mg  
 Rate: 20 DEG/MIN 100CC N2/MIN

TGA

Date: 6-Oct-83 Time: 19:44:14  
 File: SUNBURY.05  
 Operator: M. SHEN

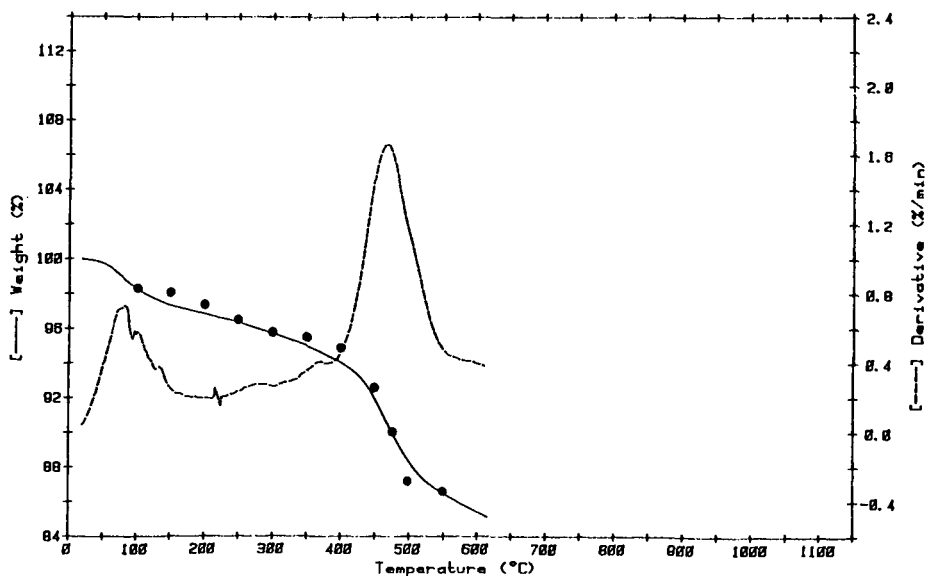


Figure 4 Non-isothermal histogram of weight loss versus temperature at 20°C/min

Sample: KENTUCKY SHALE

Date: 6-Oct-83 Time: 19:44:14

TGA

Program: TGA Kinetics V1.0

Operator: M. SHEN

Plotted: 7-Oct-83 10:12:10

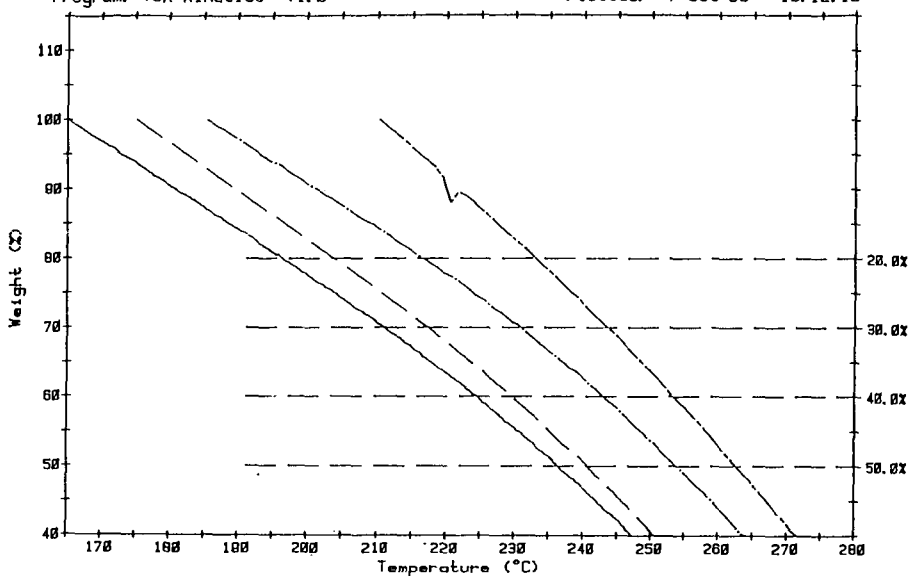


Figure 5 Extent of conversion versus temperature at various heating rates

Sample: KENTUCKY SHALE

Date: 6-Oct-83 Time: 19:44:14

TGA

Program: TGA Kinetics V1.0

Operator: M. SHEN

Plotted: 7-Oct-83 10:34:32

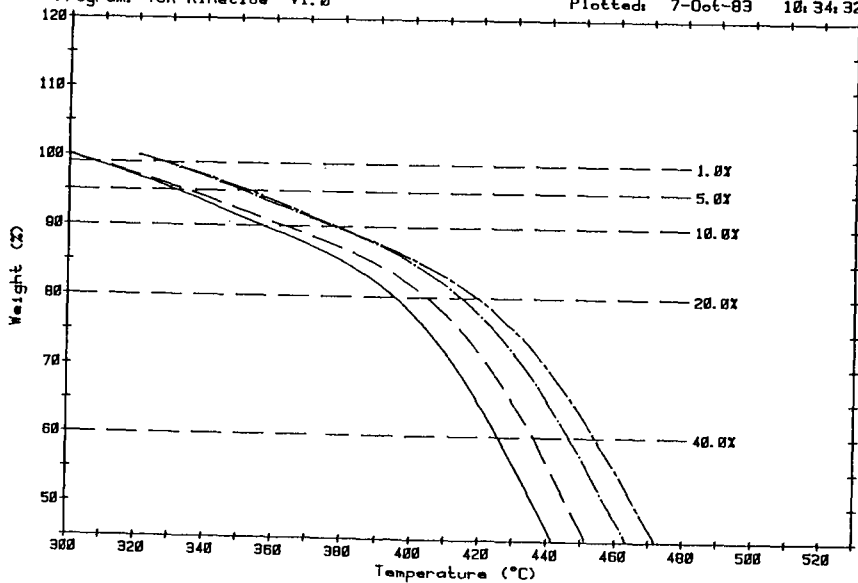


Figure 6 Extent of conversion versus temperature at various heating rates

Sample: SF-KENTUCKY SHALE  
 Size: 26.94 MG  
 Rate: 10 DEG/MIN 75CC C02/MIN  
 Program: DSC Kinetics V1.0  
 Date: 6-Oct-83 Time: 16:32:37  
 File: INSUNBURY.04  
 Operator: M. SIEN  
 Plotted: 6-Oct-83 19:48:26

DSC

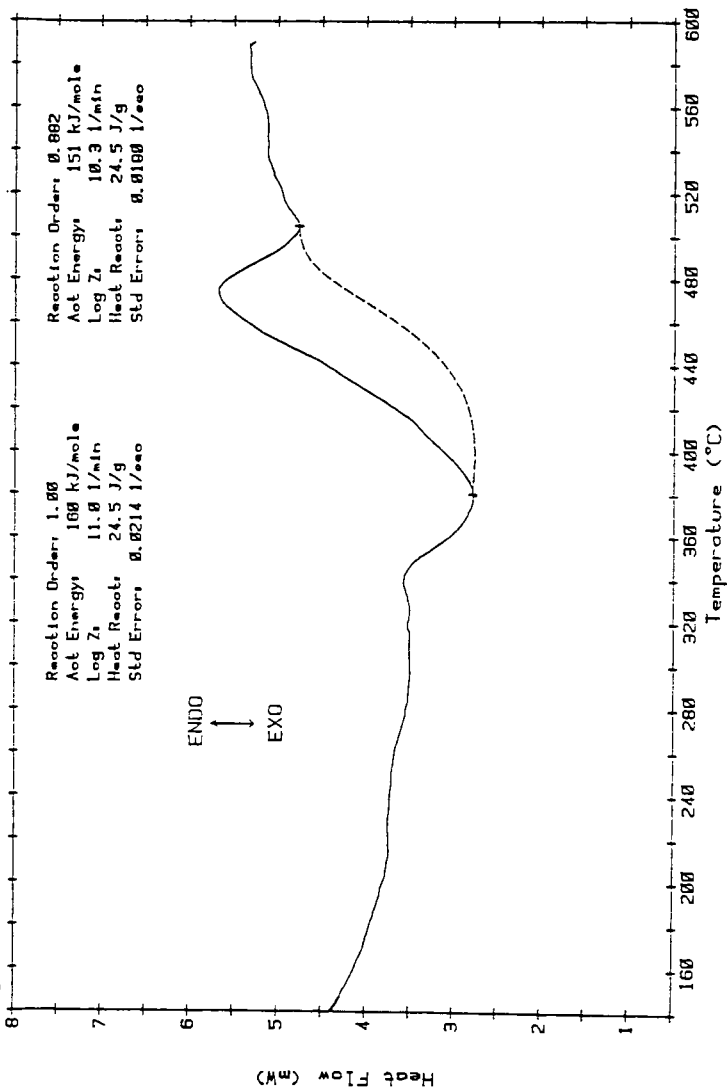


Figure 7 DSC curve for Kentucky Oil Shale at 10°C/min

data reported here.

#### NOMENCLATURE

$A_1$	frequency factor for bitumen decomposition
$A_2$	frequency factor for kerogen decomposition
$E_1$	activation energy for bitumen decomposition
$E_2$	activation energy for kerogen decomposition
$f$	fraction of mass of decomposed kerogen that yields bitumen
$H_r$	heating rate
$k_1$	kinetic constant for bitumen decomposition
$k_2$	kinetic constant for kerogen decomposition
$R$	gas constant
$t$	time
$T$	temperature
$W_1$	weight of bitumen
$W_2$	weight of kerogen
$W_{10}$	initial weight of bitumen
$W_{20}$	initial weight of kerogen
$W_i$	weight of inert material
$W$	total weight of oil shale

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